



Consumer and  
Corporate Affairs Canada

Consommation  
et Corporations Canada

# BEST AVAILABLE COPY

(11) (A) No. 1 188 891

(45) ISSUED 850618

(52) CLASS 44-9

(51) INT. CL. <sup>4</sup> C10L 1/30

## (19) (CA) CANADIAN PATENT (12)

(54) Method of and Additive for the Treatment of  
Combustibles for Accelerating Combustion and  
Inhibiting Soot Formation

(72) Kaes, Gertrude,  
Austria

(73) Granted to Lang & Co., chemischtechnische Produkte  
Kommanditgesellschaft  
Austria

(21) APPLICATION NO. 413,082

(22) FILED 821008

(30) PRIORITY DATE Austria (A 4379/81) 811012

NO. OF CLAIMS 10 - NO DRAWING

# Canada

DISTRIBUTED BY THE PATENT OFFICE, OTTAWA.  
CCA-274 (11-82)

ABSTRACT OF THE DISCLOSURE

Long-term storage of fuel oils, diesel fuels and like liquid combustibles, without oxidation or polymerization can be improved, the combustion of such combustibles accelerated and the combustion made free from soot formation with low air excess by adding to the combustible an additive which consists essentially of a first component consisting of at least one oil soluble or oil dispersible metal compound of a transition metal or an alkaline earth metal, and a second component consisting of at least one oxidation and polymerization inhibitor for hydrocarbons stable at temperatures of at least 300°C at standard pressure and having vapor pressures and decomposition temperatures above 300°C at standard pressure.

My present invention relates to an additive to combustibles for promoting combustion and for inhibiting the formation of soot (carbon black) in such combustion, as well as to a method of treating combustibles for these purposes and to a method of burning such combustibles with minimum soot formation and in an accelerated manner.

The invention is especially directed to improvements in the burning of liquid combustibles having a boiling point greater than 300°C at standard (atmospheric) pressure, to liquid fuel compositions containing the improved additive and to an improved method of burning such compositions.

In recent years, petroleum costs have risen to the point that there has been increasing interest in the efficient burning and utilization of heavy liquid combustibles such as fuel oils and diesel fuels having boiling points above 300°C at standard pressure.

However, protection of the environment has also become a growing concern and hence it has been recognized as important to carry out such combustion under conditions which minimize the production of soot (carbon black) and smoke.



79 MR

It is obvious that complete combustion to minimize soot formation and smoke pollution can be carried out with large amounts of excess air. This, however, is at the expense of efficient combustion because the heating of the large air excess represents a waste of the heat content of the fuel. Thus of greatest interest is a combustion process or system which utilizes low grade liquid combustibles with little excess air and without soot and smoke formation.

Apart from the environmental problems which arise with increased soot formation, there are major technological disadvantages. For example, the generation of incompletely burned solids rich in carbon, tends to form compact deposits impairing heat transfer through heat exchange surfaces, blocking gas flow to passages, and interfering with the dynamics of exhaust gas flow.

Such deposits are frequently found to be highly adsorptive because of the high effective surface area, leading to ready pick up of corrosive components such as sulfuric acid forming in the combustion process. This results in increased corrosion and complicates maintenance of earlier plants while contributing significantly to the operating and capital cost thereof.

Soot formation results in a gradual decrease in heating efficiency, i.e. the efficiency with which a fuel is transformed to useful heat because the deposits build up continuously, corrosion is progressive, etc.

An investigation in a large town encompassing 100,000 burner units has shown that the decrease in working efficiency amounted to 10 rel % during the heating period.

To maintain heating efficiency, therefore, continuous cleaning of all of the installations would be necessary. This is expensive and frequently unsuccessful since wear and tear of the burner, atmospheric and ambient factors such as storms, low pressure periods and the like, can cause sharply increased soot formation even immediately after a cleaning period.

Thus considerable effort has been expended in recent years to solve the problem by introducing compounds or compositions (additives) capable of reducing soot formation into liquid fuels, all with the end of allowing the reduction in the formation of deposits with a minimum of excess air.

In the combustion of fuel oils and diesel fuels the oil is usually sprayed into the combustion zone as small drops in as fine a distribution as is possible (except in the case of small carburetor ~~carburator~~ burners). The individual drops are heated quickly in this hot zone and vaporize at least partly. The vaporized hydrocarbons are mixed with the oxygen of the air surrounding the drops, thus maintaining a flame zone where corresponding combustion products are formed. While these drops pass through the combustion zone their size continuously decreases until the volatile components have been vaporized and burned.

Depending on the composition of the individual fuels and combustibles, a greater or lesser residue of non-volatile

components, consisting of high polymer organic compounds, carbon and impurities, will remain.

Strong calefaction of hydrocarbons causes cracking, i.e. larger molecules are split into smaller ones, i.e. lighter hydrocarbons, hydrogen etc. and unsaturated compounds of great activity and which are capable of further polymerization.

The resulting tarry residues and carbon burn only with greater difficulties and often incompletely - in contrast to hydrogen and the light hydrocarbons. Because of slower oxidation of these residues by atmospheric oxygen, the period in the hot combustion zone is not sufficient for complete combustion without residues.

The progress of combustion is further delayed by a screening effect which is exerted on heat transmission by the oil spray, and by the reduction of oxygen content in the immediate surroundings of the burning oil drops. During the period when heating of the oil drops and vaporization of the lighter components takes place, polymerization and pyrolysis in the remainder of the oil increases accordingly.

The progress of the chemical reactions as described above is essentially accelerated at temperatures exceeding 300°C, so that the fuel components with a higher boiling point range are more exposed to such polymerization during the combustion process. For economic reasons and reasons of availability, extra light fuel oils and diesel fuels are mixed during production so that the proportion boiling at 300°C (standard pressure) are

increased. Formerly a final boiling point of 320° to 350°C was provided for the above-mentioned products, depending on the season; nowadays the final boiling point is often at 380°C. Due to rapid development in construction and application of conversion plants for converting residues into lighter products the proportion of unsaturated and therefore thermally unstable molecules in the middle distillates available on the market is further increased. These proportions that have an increased tendency to polymerization and therefore are also a source of increased soot development.

Both tendencies, namely a higher final boiling point increasing proportion of unsaturated components, both of which can be expected to be augmented in the years to come, impede complete combustion with possibly close stoichiometric quantities of air.

In order to find a remedy, chemical additives have been investigated and tested for a long time. These additives are intended to be catalytic promoters for combustion of fuel oils and diesel fuels, i.e. promotors of complete combustion in a period as short as possible or at lower temperatures.

It is well known that metallo-organic, organic and inorganic compounds can be used as additives promoting combustion. Such metallo-organic compounds have been used in certain cases as catalysts for combustion of hydrocarbons, because on the one hand they can be dissolved or dispersed in oil-soluble or oil-dispersible form, and on the other hand as

compounds of transition metals and/or alkaline earth metals have been effective as catalysts for combustion.

B

A hypothesis as to the effect of alkaline earth (calcium, strontium, barium) metals and probably also of molybdenum as catalysts for combustion suggest that these act in gas phase catalysis by splitting up molecular hydrogen and water molecules into hydrogen atoms. The latter quickly react with the water vapor, developing hydroxide radicals which react with the carbon of the soot.

The transition metals, however, seem to become effective as metal oxides, accelerating development of CO and CO<sub>2</sub> from carbon in the combustion zone which is cooler and contains more oxygen. It is wellknown and measurable that combustion of carbon (soot) can take place at lower temperatures if catalysts of the transition metals are present in a suitable form. Simultaneous application of alkaline earth and transition metals for combustion has proven to be of advantage, because both groups can develop their catalytic effects in turn in the hot zone and in the zone which is subsequently colder, but contains more oxygen.

Addition of pure organic compounds (without a metal content) has also been tested, but addition of the usual small quantities to be added has not resulted in a significant effect in promoting combustion. Thus alcohols, phenols, esters, low aromatic compounds, hydrazine derivatives, organic amines, naphthonic acids and carbonic acids were tested, without significant increase of combustion or influence on soot development.

Another problem in connection with the use of fuel oils and diesel fuels (made of mineral oils or synthetic oils) is their stability for storage purposes.

It is desirable that the properties of these hydrocarbons not be impaired in the course of time due to oxidation and polymerization. For this purpose inhibitors have been widely used in practice, especially for light fuels and lubricating oils but also with fuel oils and diesel fuels.

A special problem of storage arises with products containing metallo-organic compounds of transition metals, especially copper, manganese, cobalt, nickel and iron compounds, because these compounds accelerate deterioration, especially with unsaturated hydrocarbons.

It has also been found that a deterioration can occur even in the presence of such metals in complexes, e.g. if methylcyclopentadienyl manganese tricarbonyl (MMT) or dicyclopentadienyl iron (Ferrocene) is added to middle distillates and heavy fuel oils.

A wellknown short-time method for determination of stability of middle distillates is the accelerated stability test (or EDM Diesel test, Union Pacific or Nalco or DuPont test) at 149°C (300° Fahrenheit). This test determines the relative stability of middle distillates under short-time aging conditions at high temperatures and with air admission.

The process consists in aging of the sample of distillate at 149°C (300° Fahrenheit) for 90 minutes with air

118891

9 MR

admission; the residues developed are filtered. The filter coating is evaluated in numbers from 1 to 20 according to thickness and color which gives a comparison of the individual distillates' stability to aging. The lower the evaluation number, the more stable is the distillate, a numer up to 7 being still satisfactory. In addition to the filter evaluation, the color of the distillate before and after aging is determined according to ASTM (D - 1500 - 58%) which also permits a relative evaluation of stability.

Application of this test showed a remarkable increase of the evaluation numbers after aging whenever copper, manganese, cobalt, nickel and iron compounds had been added to the distillates (e.g. naphthenates, octoates, sulphonates, but also complexed compounds). Increases for several points occurred, depending on the composition of the medium heavy distillate, with a proportion of 10 to 25 parts of the above-mentioned metals in one million parts of hydrocarbon (ppm).

In practice these fuels are exposed to higher temperatures than the usual storage temperatures when excess fuel oil is returned from the burner to the tank, which further increases the tendency to polymerization and oxidation and often accelerates such tendencies, causing a deterioration of quality of fuel oils.

It appears therefore that, according to the actual state of technical science, combustion can be improved by catalytic oil-soluble and/or oil-dispersible metal compounds, which

**118891**

simultaneously creates the disadvantage of increased aging of the treated fuel oils and diesel fuels. So in many cases the economic advantage of combustion promotion is destroyed and changed into even greater disadvantages, like obstruction of  
5 burners and piping systems.

The present invention provides an additive for fuel oils and diesel fuels and other liquid combustibles and motor fuels which inhibits polymerization at  
10 temperatures of 300°C and higher.

The present invention also provides an improved fuel or diesel oil composition, capable of long-term storage and having good resistance to oxidation and polymerization at high temperatures, but also improved combustion and reduced tendency  
15 to soot formation.

The present invention still further provides an improved method of burning fuel oils and diesel fuels and other liquid combustibles, which nevertheless also improves the storage life of the combustible and inhibits polymerization at  
20 temperatures of 300°C and higher, thereby preventing reactions which might result in generation of high molecular weight tarry hydrocarbons which can contain carcinogenic polycyclic aromatics.

In order to be able to inhibit polymerization even at  
25 temperatures of 300°C and higher, the inhibitors do not decompose, boil, sublimate or evaporate at this temperature at standard pressure.



Therefore the wellknown oxidation and polymerization inhibitors for stabilization of fuel oils and distillates cannot be applied for the purposes of the invention because they do not comply with the demands. So 2,4-dimethyl-6-tert-butyl phenol, 2,6-di-tert-butyl-p-cresol (BHT), sterically hindered xylenols and trimethyl phenols, butylized hydroxy anisols (BHA), mono-tert-butyl hydrochinon (TBHQ), para-cresols and aromatic amines are frequently used for storage stabilization of light and middle distillates. These inhibitors are suitable only for temperature ranges up to 150°C.

For stabilizing synthetics, lubricating oils and asphalts oxidation and polymerization inhibitors have already been applied which are also suitable for higher temperatures. A wellknown aging preventive for heat-resistant rubber articles is e.g. the zinc salt of 2-mercaptop- benzimidazol. But this inhibitor is also decomposed at temperatures about 300°C and is not suitable for higher temperatures.

The additive of this invention comprises at least one oil-soluble and/or dispersible compound of a transition metal and/or alkaline earth metal as well as one of several inhibitors against polymerization and oxidation of hydrocarbons; these inhibitors are heat-resistant and can be exposed to temperatures of 300°C and higher - at least for a short time - without losing their polymerization inhibiting effects, due to their vapor pressure and/or their temperature of decomposition (at standard pressure). The liquid combustible and motor fuel of this

79 MR

invention is characterized by a metal content amounting to 0.1 to 100 parts by weight per one million parts by weight of the mentioned combustibles and motor fuels.

More specifically, the additive of the invention, which is used in an amount corresponding to 0.1 to 1000 parts by weight metal ppm of the fuel or diesel oil, comprises a metal component (compound) distributable in the fuel or diesel oil and selected from the group which consists of iron, manganese, molybdenum, cobalt, nickel, calcium, strontium and barium, and preferably two or more of such compounds, an organic inhibitor component selected from the group which consists of a heat-stable alkylphenol, aminophenol, amine, dithiophosphate, dithiocarbamate and imidazole, preferably two or more of such inhibitor compounds, and at least one inorganic inhibitor selected from the group which consists of the oxides and hydroxides of aluminum, magnesium and silicon.

The additive of this invention on the one hand improves storing properties of the above-mentioned combustibles, and on the other hand the polymerizations as described above which normally are considerably accelerated at temperatures above 300°C are inhibited effectively.

At the same time the advantage of a more complete combustion is achieved, even with less excess air. This is the more important as the above-mentioned tendency increases to use heavy mixtures and products from conversion plants, especially catalytic and thermic crackers and coking plants, with fuel oils and diesel fuels.

The organic polymerization inhibitors used in accordance with the present invention are effective also at temperatures above 300°C. They are not only heat-resistant at such high temperatures until the hydrocarbon drop to be burnt has passed the combustion zone, but also provide for effective protection against oxidation for fuel oils and diesel fuels at the usual normal storing temperatures, which is a great advantage. Such inhibitors are e.g. high boiling phenols with long-chained, sterically hindered alkyl groups, e.g. nonyl. But also organic amine compounds of higher molecular weight, e.g. N-phenyl-2-naphthylamine, satisfy this condition. In practice it is of course necessary always to consider possible carcinogenic effects, and additives known not to be detrimental to health have to be preferred, although usually fuel oils and diesel fuels should not come into contact with the skin or with foodstuffs.

Selected metal (e.g. zinc, molybdenum)-alkyl-dithiophosphates, -dithiocarbamates and imidazoles, as well as other metal compounds can also satisfy the requirements for heat stability and therefore are suitable inhibitors. Inhibitors on the basis of high-alkyl or polymer sterically hindered phenol compounds have proven to be especially economical and do not cause any increase of detrimental matters due to SO<sub>2</sub>/SO<sub>3</sub> or nitric oxides, phosphorus compounds, etc. in the exhaust gas, which is of great advantage.

EXAMPLESExample 1

Dark fuel oil with the following analytic data is burned in a Pieren furnace with Olymp 8D and Unitherm mat 5 burners - with and without the additive according to this invention.

Specific gravity at 15°C	0.920 g/ml
flash point P.M.	120°C
solidification point	-15°C
viscosity at 50°C	20.4 cst
sulphur total	0.92 wt %
coking residue and	
Conradson	4.2 wt %
ash content	0.05 wt %
water content	0.2 wt %
net calorific value	41 750 kJ/kg

In combustion of this fuel oil without additive in the "Olymp" burner the smoke spot number (Bacharach) amounted to 3, with an air number of 1.4.

In the "Unitherm" burner a smoke spot number of 3.3 was measured while the air number remained the same.

Furnace efficiency, measured with the calorimeters, was 76.0 - 76.3% and 75.8 - 76.2% in the mentioned burners.

Addition of 1 part by weight of an additive of the following composition to 1000 parts by weight of this dark fuel oil resulted in an improved smoke spot number (with constant air number of 1.4) amounting to 1.5 in the "Olymp" burner and 1.2 in the "Unitherm" burner.

1188891

179 MR

The furnace efficiencies of the fuel oil containing additives were 79.5 to 80.0% ("Olymp" burner) and 82.0 - 83.0% ("Unitherm" burner), using the same calorimeter. The average efficiency gain amounted to 3.6 resp. 6.5% due to the additive.

The composition of the additive according to this invention was as follows:

30 wt % oil-soluble barium petrol sulphonate/oil dispersible barium carbonate with a total proportion of 4.2 wt % Ba  
40 wt % oil-soluble calcium petrol sulphonate/oil dispersible calcium carbonate with a total proportion of 4.88 wt % Ca  
6 wt % alkylated sterically hindered phenol with a mol weight of 280 and a vapor pressure of 270 torr at 300°C; 6.0 wt %  
24 wt % aromatic carbohydrates with a boiling range of 180° ---  
230°C and flash point P.M. of 60°C

Additive according to the present invention: 100%.

Example 2

Extra light clear fuel oil with the following analytic data is burned with and without additive according to this invention in a "Vossmann", Duo Parola-E, steel furnace with "Weishaupt" oil burner type WL 2/3 with a thermal capacity of max 81 kW.

Specific gravity at 15°C	0.835 g/ml
viscosity	4.8 cst
flash point A.P.	70°C
sulphur	0.38 wt %
solidification point	-5°C
net calorific value	43 076 kJ/kg

1188891

In combustion of this middle distillate without additive, a smoke spot number of 2.9 - 3.2 (Bacharach) was determined with an exhaust gas proportion of 12.3 - 12.4% CO<sub>2</sub>, 16.4% CO<sub>2</sub> + O<sub>2</sub>, less than 0.01% CO.

With a composition of flue gases containing 12.6% CO<sub>2</sub>, 16.1 - 16.2% CO<sub>2</sub> + O<sub>2</sub>, less than 0.01% CO the smoke spot number was 4.

Addition of an additive in the following composition (proportion: 1 part by weight of additive to 2500 parts by weight of extra light fuel oil) under analogous conditions of combustion resulted in a reduction of the smoke spot number to 1.06, i.e. an improvement by 2 points (average), the exhaust gas containing 12.3 - 12.4% CO<sub>2</sub> and 16.4% CO<sub>2</sub> + O<sub>2</sub>, less than 0.01% CO.

With a proportion of 12.6% CO<sub>2</sub>, 16.1 - 16.2% CO<sub>2</sub> + O<sub>2</sub>, less than 0.01% CO in the flue gases, the smoke spot number had an average value of 1.63, i.e. an improvement by approximately 2.4 points.

The additive contained:

Barium petrol sulphonate/barium carbonate

with a total proportion of

3.35 wt % Ba

Ferrocene with a total content of

2.10 wt % Fe

alkylated sterically hindered

phenol with a mol weight of 280

and a vapor pressure of 270 torr  
at 300°C

5.00 wt %

aromatic solvents to 100%

118891

9 MR

Example 3

Gas oil with the following analytic data was burned under the conditions of Example 2 with and without additive

Specific gravity at 15°C	0.845 g/ml
flash point P.M.	65°C
cold filter plugging point	-18°C
viscosity at 20°C	5.1 cst
total sulphur	0.25 wt %
diesel index	52
distillation range up to 350°C	92 vol %

This gas oil complies with the European regulations for application as a diesel fuel.

The following additives according to this invention were added to the gas oil, containing alkylated phenol acc. to Examples 1 and 2, sterically hindered tert-nonyl-cresoles, N-phenyl-2-naphthylamines and other high-vaporizing polymerization and oxidation inhibitors with a boiling point (boiling range) exceeding 300°C at standard pressure. Addition of the ready additive was made in a proportion of 1 part by weight of additive to 2000 parts by weight of gas oil. With the following proportions of metals in the additive subject to this invention, the following improvements of the smoke spot number were achieved:

118891

Composition of Additive	reduction of smoke
	<u>spot number (Bacharach)</u>

Metal contents	polymerization inhibitor acc. <u>to invention</u>	
a) 4.23 wt % Ba	5 wt %	-1.6 points
b) 3.36 wt % Ca and 0.72 wt % Ba	5 wt %	-1.5 points
c) 3.81 wt % Ba and 1.2 wt % Fe	5 wt %	-2.0 points
d) 7.05 wt % Ba	5 wt %	-1.9 points
e) 5.19 wt % Ba and 4.48 wt % Ca	5 wt %	-2.0 points
f) 6.35 wt % Ba and 1 wt % Fe	5 wt %	-2.7 points
g) 3.38 wt % Fe	5 wt %	-2.0 points
h) 3.05 wt % Cu	5 wt %	-2.2 points
i) 4.8 wt % Co	5 wt %	-2.8 points
j) 5.0 wt % Mn	5 wt %	-2.5 points

It can be seen clearly that all combinations of the additive essentially promote combustion and that the original smoke spot numbers could be dramatically reduced from 3 - 4

to partly below. This results in conditions for combustion with less soot involvement, even with reduced excess air, with corresponding improvement of thermal efficiency.

Example 4

B. The polymerization and oxidation inhibitors subject to this invention having a temperature stability above 300°C result also in very good effects protecting against aging at low (storing) temperatures.

A coker gas oil with the following analytic data was applied

Specific gravity at 15°C                    0.858 g/ml

flash point P.M.                            62°C

sulphur content                            0.38 wt %

Pour point                                    -12°C

viscosity at 20°C                        3.5 cst

undissolved matter                        150 mg/kg

This coker gas oil (without additive) was exposed to the accelerated aging test at 149°C (300° Fahrenheit) as described above for 90 minutes. The color number was 9.

Presence of Ferrocene in a quantity that the Fe-content of the product amounted to 15 ppm caused an increase of the color number to 14, presence of 15 ppm manganese (of MMT) increased the color number to 16, 16 ppm copper (of copper naphthenate) caused an increase to 18.

Addition of additives in accordance with this invention containing each 3 wt % of iron (in one case of Ferrocene, in the

118891

179 MR

other case of iron naphthenate) and 6 wt % of alkylated phenols according to Examples 1 and 2 as inhibitors, for completion up to 100% heavy petroleum blend - a proportion of 1 part by weight of additive to 1000 parts by weight of coker gas oil - resulted in a Fe content of 15 ppm in the product in a comparison test with the additive subject to this invention. The same accelerated aging test (see above) showed color numbers of 3 - 4 with these coker gas oils containing additives.

Aggravation of the aging conditions (application time double to 180 minutes) at 149°C (300° Fahrenheit) resulted in color numbers of 5. It appeared that due to application of the additives in accordance with this invention the desired aging number below 7 could also be achieved for middle distillates of thermal conversion.

Example 5

The coker gas oil without additive as described in Example 4 was used as a diesel fuel in trucks. In practice, however, operation of these vehicles with that product was not possible because these diesel engines developed heavy unbearable smoke, not only under full load, but also under normal operating conditions; this may be due to the high proportion of aromatic compounds and unsaturated hydrocarbons.

An additive in accordance with this invention, consisting of 15 wt % MMT, 20 wt % alkylated phenols according to Examples 1 and 2, and 65 wt % of paraffin base petroleum, was added to 700 parts by weight of coker gas oil in a proportion of 1 part by weight of additive.

The manganese content amounted to 52.8 ppm, the content of high boiling alkylated phenols in the coker gas oil was 28.6 ppm. Smoke development of the diesel engines operated with this motor fuel was reduced dramatically and amounted to an average of 5 20 Hartridge units. The residues in the combustion cylinders of the engines operated with this substance were negligible, even after an application for several months, and the injection was in an excellent condition.

#### Example 6

10 Residual fuel oils, containing heavy visbreaker proportions had the following analytic data:

Specific gravity at 15°C	0.995 g/ml
viscosity at 50°C	20° Engler
flash point	160°C
coking residue (Conradson)	14 wt %
solidification point	+18°C
sulphur content	5.5 wt %

15 Combustion of this residual oil without an additive with little soot development was possible only with a very high excess 20. of air and exactly adjustable burners, mostly with injection of water vapor.

20. 100 ppm manganese (of manganese naphthenate) was added to this heavy residual oil, as well as silicon dioxide, obtained from silicon tetrachloride by means of flame hydrolysis, with a BET surface of app. 200 (supplied under the trademark Aerosil 200), in a quantity of 50 ppm, plus aluminium oxide with a BET surface of app. 100 (aluminium oxide C), also in a quantity of 30 ppm.

1188891

379 MR

Combustion in standard industrial burners with little soot development was possible without difficulties with air numbers about 1.2 and lower, when the residue oil, provided with an additive as described above, was applied.

The silanol groups at the surface of high disperse silicic acid as well as analogous aluminum hydroxides in high disperse aluminum oxide seem to be responsible for inhibiting polymerization at temperatures exceeding 300°C, while the

B manganese seems to have been a catalyst promoting combustion of carbon <sup>or</sup> resp. particles enriched with carbon in the colder combustion zone. The inorganic polymerization inhibitors according to this invention were thus also applied successfully.

79 MR

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An additive for promoting combustion of a liquid combustible, preventing soot formation in the combustion of said liquid combustible and stabilizing said liquid combustible against oxidation and polymerization at elevated temperatures upon storage, said additive comprising:

B a first component consisting of at least one oil soluble or oil dispersible <sup>Organic</sup> metal compound of a transition <sup>metal</sup> metal or an alkaline earth metal; and

a second component consisting of at least one oxidation and polymerization inhibitor for hydrocarbons stable at temperatures of at least 300°C at standard pressure and having vapor pressures and decomposition temperatures above 300°C at standard pressure.

2. The additive defined in claim 1 wherein said components are in a ratio such that the weight ratio of said metal to said inhibitor is 1:0.1 to 10.

3. The additive defined in claim 2 wherein said first components comprises at least one compound of iron, manganese, nickel, molybdenum, cobalt or copper.

4. The additive defined in claim 3 wherein said first component further comprises at least one compound of calcium, strontium or barium.

79 MR

5. The additive defined in claim 3 or claim 4 wherein said second component comprises an organic inhibitor selected from the group of heat-stable alkylphenols, amines, aminophenols, dithiophosphates, dithiocarbamates or imidazoles.

6. The additive defined in claim 3 or claim 4 wherein said second component comprises an inorganic inhibitor in the form of at least one oil dispersible oxide or hydroxide of aluminum, magnesium or silicon.

7. A liquid combustible composition capable of long-term storage, accelerated combustion and combustion without soot formation comprising 0.1 to 1000 parts by weight of metal content of the additive defined in claim 1 per million parts by weight of the liquid combustible.

8. A method of improving the combustion of a liquid combustible comprising adding to said liquid combustible an additive in an amount of 0.1 to 1000 parts by weight metal content of the additive per million parts by weight of the liquid combustible, said additive being defined in claim 1.

9. A method of improving the storage life of a liquid combustible which comprises adding an additive in an amount of 0.1 to 1000 parts by weight metal content of the additive per million parts by weight of the liquid combustible, said additive being defined in claim 1.

1188891

10. An additive for promoting combustion of a liquid combustible, preventing soot formation in the combustion of said liquid combustible and stabilizing said liquid combustible against oxidation and polymerization at elevated temperatures upon storage, said additive comprising: a first component consisting of at least one oil soluble or oil dispersible organic compound of a transition metal or an alkaline earth metal; and a second component consisting of at least one oxidation and polymerization inhibitor for hydrocarbons stable at temperatures of at least 300°C at standard pressure and having vapor pressures and decomposition temperatures above 300°C at standard pressure and selected from the group which consists of: organic inhibitors selected from the group of heat-stable alkylphenols, amines, amino-phenols, dithiophosphates, dithiocarbamates and imidazoles, and inorganic inhibitors in the form of at least one oil dispersible oxide or hydroxide of aluminum, magnesium or silicon.



24

B

SUBSTITUTE  
*REEMPLACEMENT*

there are NO DRAWINGS

*il n'y a PAS DE DESSINS*

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**